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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY WASHINGTON, D.C. 20460

JAN 1 6 1987

OFFICE OF PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT:

EPA Reg. No. 279-3026 and 279-3027 Cypermethrin: Update on the presence of hydrogen cyanide in the headspace of the products AMMO® Technical Insecticide

and AMMO® 2.5 EC Insecticide.

TOX CHEM No. 271DD TOX PROJECT No. 7-0241 Record No. 186740

186741

FROM:

John Doherty Soutonery (15/87

Toxicology Branch

Hazard Evaluation Division (TS-769)

TO:

George LaRocca

Product Manager 15

Registration Division (TS-767)

and

Exposure Assessment Branch

Hazard Evaluation Division (TS-769)

THRU:

Edwin Budd Section Head

Toxicology Branch

Hazard Evaluation Division (TS-769)

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Background:

The FMC Corporation (Philadelphia, Pa.) has previously informed EPA that their products AMMO® Technical Insecticide (EPA Reg. No. 279-3026) and AMMO® 2.5 EC Insecticide (EPA Reg. No. 279-3027) contain detectable amounts of hydrogen cyanide (HCN) in the headspace of their containers (refer to the review by J.D. Doherty dated June 3, 1986 under these EPA Reg. Nos.) In the previous Toxicology Branch (TB) review, it was indicated that the levels of hydrogen cyanide reported were below levels which would be expected to result in a hazard. The registrant was, however, advised to continue to investigate the causes for the hydrogen cyanide production and devise methods to reduce or eliminate it.

W/F

In the current submission, the registrant has submitted information on quantitative hydrogen cyanide (HCN) measurements using commercial devices, equilibrium conditions (for HCN in liquid and vapor phases), and hazard evaluation related to vapors in the headspace and accidental spills.

TB Comments

- 1. TB cannot comment on the <u>chemical methods</u> used to quantitate for hydrogen cyanide or the <u>exposure</u> resulting from various "actual and simulated" circumstances. <u>This information</u> should be forwarded to Exposure Assessment Branch (EAB) for review.
- 2. Mr. Stewart's letter (dated August 15, 1986) states that the HCN measurements reported in the first letter for AMMO formulations were wrong as a result of the analytical procedures used. The concentrations in the formulations would be expected to be 15 times lower than reported earlier based on equilibrium studies. TB needs EAB's assessment regarding the recently submitted data before any conclusions or recommendations can be made.
- 3. The confirmation that the HCN levels are in fact lower than the levels previously reported would further deminish a potential hazard of HCN poisoning resulting from this gas in the head space of the containers. The levels previously reported were not considered by TB to represent a significant hazard (refer to J.D. Doherty memo dated June 3, 1986).



. TB should be informed of EAB's review of the procedures used to analyze for HCN and their (EAB's) opinion regarding the factors which may result in a buildup of HCN in the headspaces of the containers as well as factors responsible for the spontaneous production of HCN in solutions containing cypermethrin.

TB will provide the appropriate comments related to the potential hazards of HCN in the AMMO products pending receipt and review of the EAB memo.

Representative

Accepted Uses

22. Labels Showing

Attached

23. Date Returned to RD

(to be completed by

24. Include an Original and 4 (four)

for Each Branch Checked for

Copies of This Completed Form

EPA Form 8570-13 (Rev. 11-81) PREVIOUS EDITIONS ARE OBSOLETE.

Confidential

21. Statement of

Formula

Label Submitted

20. with Application

Attached

Attachment

FMC Corporation

Agricultural Chemical Group 2000 Market Street Philadelphia Pennsylvania 19103 215 299 6000

August 15, 1986

Mr. George T. LaRocca (PM-15) Registration Division (OPP) (TS-767C) U.S. Environmental Protection Agency 401 M Street. S.W. Washington, DC 20460

Dear Mr. LaRocca:

Subject: Ammo® Technical Insecticide EPA Registration No. 279-3026

Ammo® 2.5EC Insecticide

EPA Registration No. 279-3027

Presence of Hydrogen Cyanide in Ammo Products

FMC Corporation submits the following information to provide an update on the status of our investigations concerning hydrogen cyanide (HCN) in Ammo products. We include information on quantitative HCN measurements using commercial devices, equilibrium conditions, and hazard evaluation. Our research has resulted in the following conclusions:

- o There are several commercial measuring devices for HCN. FMC ... has determined that while each has some inaccuracy, the Gastec® Tube would be the recommended choice. Gastec tubes have a tendency to give high readings, but that is preferable to low or erratic readings.
- o HCN measurements reported in our first letter for Ammo formulations were wrong. The erroneous values reported earlier were caused by the analytical procedure. The equilibrium studies indicate that concentrations in the formulation are about 15 times lower than reported earlier.
- o The potential for a hazardous release of HCN from either headspaces or as the result of a leak or spill was evaluated. in actual and/or simulated circumstances. The results show that hazardous levels did not occur during routine operations or in the potential accidental releases.

A detailed account of our findings follows and is divided into discussions of commercial HCN detectors, liquid-vapor phase equilibria, and the potential for hazardous release.

Evaluation of Commercial HCN Detectors

Gastec detector tubes were used for most determinations of vapor phase HCN. These tubes are designed for testing workplace environments where the actual "sample" is normally of very large volume, so we always used the tubes where the sample volume was at least 500 mL and took no more than 100 mL for analysis; sampling was done in a way that the air entering the container to replace the 100 mL withdrawn had minimal effect. A limited amount of analyses were done with MSA tubes and GC. A few experiments were also done in which HCN was trapped in aqueous NaOH and then CN- concentration was determined with an ion selective electrode. Although Gastec tubes appear to give slight positive error in HCN levels and show, on occasion, a suspicious discoloration, they are an expedient and adequate way to estimate HCN. The following is a comparison of results obtained with Gastec tubes to results obtained with the other mentioned techniques.

Comparison of Gastec Tubes to MSA Tubes Using HCN/N2

A Metronics Model 450 Dynacalibrator was used to prepare a standard HCN(g) sample. Accordingly, a Dynacal permeation tube (#101-150-5300) was used to generate an atmosphere of 15 uL HCN/L in a 1 L two-necked flask. Gas samples of 100 mL volume were removed from the flask by means of either a Gastec sampler or an MSA sampler.

The following results were obtained:

HCN/uL.L-1				
 Actual (+4)	Foun Gastec	d MSA	Analyst	
15	19	i, e e e e e e e e e e e e e e e e e e e	1	
15 15	17 20		2	
15	19.5		2 2 2 2	
15 15		10	2	
15		7	2	

The average Gastec value, 19 uL/L, was 27% higher than the standard. The manufacturer of Gastec tubes claims an accuracy of \pm 25%. The MSA tubes, on the other hand, gave values that were about 47% too low. In addition, MSA tubes gave a more diffuse stain and were hard to read. It should be emphasized that these conclusions apply to the tubes in our possession and may not necessarily apply to all lots of MSA tubes.

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Comparison of Gastec tubes to Ion Selective Electrode using Ammo 2.5 EC Formulation head space

During equilibration studies, the vapor phase over Ammo 2.5 EC was isolated from the liquid phase, then swept into caustic solution and finally the solution was analyzed potentiometrically with an ion selective electrode. Results obtained were 50 ppm uL/L by electrode and 61 uL/L by Gastec tube.

Draeger Tubes

Our laboratory at the Baltimore manufacturing plant feels that the Draeger sampling apparatus gives highly imprecise results. The sampling pump is a bellows-type pump that requires compression by hand; the amount of vapor drawn through the detector tube is proportional to how completely the pump is compressed. Since this varies with each individual analyst, HCN values tend to be highly variable.

Gas Chromatography

The feasibility of using gas chromatography as an alternative to detector tubes for measuring HCN in the cypermethrin vapor space is currently being evaluated. While we have found that there is interference from carbon monoxide using thermal conductivity detection, flame ionization detection (FID) does not suffer from this interference. Work is in progress to determine if a reliable GC method can be developed employing FID.

Conclusion

Gastec tubes appear to be the best alternative at this time for routine determination of HCN in vapor phases over cypermethrin-containing products. Although there is evidence that Gastec tubes may be slightly positively biased and, in fact, suspicious discoloration is sometimes observed, the values obtained are adequate to establish the severity of any HCN presence. We do not recommend using Draeger tubes and we would caution any user of MSA tubes that these tubes may give low results.

Liquid-Vapor Phase HCN Equilibration Studies

When hydrogen cyanide gas was detected in the vapor phase over cypermethrin-related materials, it became necessary that certain questions be answered. For one, what did a detected level of 50 or 100 ppm (v/v) in the headspace mean in terms of the amount of HCN in solution? Another question was what would happen to air quality if cypermethrin-related materials were accidently spilled in an unventilated area? These and a variety of other questions were addressed in a number of experiments including investigations into the source(s) of HCN and means to control HCN release.

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Theory

Consider a closed system composed of a liquid phase (cypermethrin technical or formulated goods) and vapor phase.

Let m = mass of the liquid phase (grams)

 V_h = volume of the "headspace"

 C_1 = micrograms HCN per gram liquid phase or ppm (w/w)

 C_h = microliters of HCN per liter of headspace or ppm (v/v)

 Q_0 = total mass (ug) of HCN in system

then

$$Q_0 = mC_1 + 1.105 V_h C_h$$

where

1.105 = conversion factor, ul to ug, i.e.,

27.03g HCN

1 mole HCN

mole HCN

24.463L at 25°C, 1 atmosphere

From the distribution law, and Henry's law in particular, we can write:

$$K = \frac{C_h}{C_1}$$

or

$$Q_0 = mC_h/K + 1.105V_hC_h$$

= $C_h(m/K + 1.105V_h)$ (1)

$$C_{h} = \frac{KQ_{o}}{1 + 1.105KV_{h}/m}$$
 (2)

This equation shows, and experiments verify, that the headspace concentration varies for a particular system with the ratio of headspace volume to mass of liquid phase when the amount of HCN is constant.

Suppose the same system is now changed only by increasing the "headspace". This would be the case, for example, if a container of material were spilled in a room.

Let V = new volume of the vapor phase

C_V = vapor phase concentration of HCN is the new volume

Since Q_0 is constant here, Equation (1) gives

$$C_h(m/K + 1.105V_h) = C_V(M/K + 1.105V)$$

or

$$C_V = C_h \frac{1 + 1.105 \text{KV}_h/\text{m}}{1 + 1.105 \text{KV}/\text{m}}$$
 (3)

Evaluation of K

The concentration of HCN in the vapor phase is in equilibrium with the HCN in solution for static systems. Methods of analysis, therefore, needed to be chosen that avoided disturbing the equilibrium. Moreover, care was needed to avoid inadvertent formation of HCN during analysis. In order to evaluate K, an equilibration experiment was designed.

Figure 1 shows the apparatus used to evaluate K. The apparatus was first swept with nitrogen. Then a weighed sample of formulation (ca. 20g) was placed in the saturator. To achieve equilibrium, stopcocks 1, 2, and 3 were positioned so that the internal atmosphere of the apparatus was circulated in the cyclic direction IBCEFHI for several hours. To measure the amount of HCN in the reservoir, the pump was turned off, a caustic scrubber (0.1N NaOH) was attached at G, a nitrogen line was connected at D, and stopcocks 2 and 3 were positioned so that external nitrogen would flow in the direction DEFG. The amount of HCN in the liquid phase was then measured by connecting a caustic scrubber at D, a nitrogen inlet at A, and positioning stopcocks 1 and 2 so that nitrogen flow would be in the direction ABCD.

Internal volumes of the apparatus were measured with water.

If
$$V_1$$
 = gas phase volume from B to C = 0.149 L

$$V_2$$
 = volume from E to F = 1.080 L

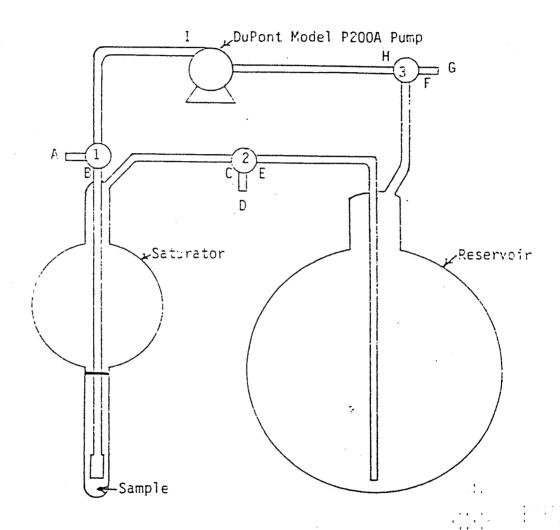
then

$$C_h = \frac{(\text{ug HHCN in scrubber at G})/1.105}{V_2}$$

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Figure

Equilibration Apparatus



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Discussion

In earlier work, Gastec tubes had been used to determine headspace concentrations of HCN over cypermethrin-related liquids. Early attempts were also made to estimate HCN in solution by preparing an emulsion of sample in 0.1N NaOH and measuring the cyanide ion concentration potentiometrically (ion selective electrode). Although there was no information available as to what caustic solutions would do, especially during short time intervals between emulsion preparation and analysis, there was strong suspicion that this approach would cause positive error in HCN measurements. This earlier work had suggested that the distribution coefficient, K, was close to unity.

The equilibration studies described here revealed that the distribution coefficient of HCN in vapor phase compared to an associated liquid phase has a value of about 15 for Ammo® 2.5 EC Insecticide. Attempts were also made to evaluate the coefficient for Ammo technical, but this material is too viscous at room temperature to permit an efficient flow of nitrogen in the apparatus. Nevertheless the results obtained indicated that K for Ammo technical may be several times larger than the value for Ammo 2.5 EC.

Using K = 15, Equation 3 becomes

$$C_V = C_h \frac{1 + 1.16 \text{ V}_h/m}{1 + 1.16 \text{V}/m}$$

and a number of predictions can be made. For example, suppose the contents of a 55 gallon drum of Ammo 2.5 EC were spilled in a room of Volume V. Suppose further that the average headspace in a 55 gallon drum is 7 liters. In general, then

$$C_V = \frac{C_h}{1 + 7.91 \times 10^{-5}V}$$

i.e., $m = 55 \text{ gal } \times 8.4 \text{ lb/gal } \times 454 \text{ g/lb} = 2.10 \times 10^5 \text{g}$.

For a 40 ft. x 20 ft. x 20 ft. room,

$$V = (40)(20)(20) \text{ ft}^3 \times 28.32 \text{L/ft}^3 = 4.53 \times 10^5 \text{L}$$

and then

$$C_V = C_h/36.8$$

Therefore at room temperature, if the drum headspace had contained 50 uL/L before a spill, the air in the room would contain 1.4 uL/L; at equilibrium.

(0 {} Equation (1) can be used to explain the observation that when the headspace of a drum is swept with nitrogen to remove HCN, the concentration of HCN in the headspace is reestablished after a period of time. To see this, assume the headspace of a 55 gallon drum of Ammo 2.5 EC contains 50 uL/L before it is swept with nitrogen. Most of the HCN is in the liquid phase, i.e.,

 $Q_0 = C_h m/K + 1.105 V_h C_h$ = 50(2.10 x 10⁵/15) + 1.105(7)(50) = 7.0 x 10⁵ (in sol'n) + 387 (in vapor phase)

i.e., over 99.9% is in solution. This means that the liquid acts as a reservoir so that when equilibrium is reestablished, the headspace concentration will be only slightly decreased from what it was before flushing.

Although most of the HCN is in the liquid phase, the quantity dissolved is still small. For example, suppose someone ingested 100 g Ammo 2.5 EC which had shown a headspace concentration of 50 uL.L-1. This material would have a solution concentration of 50/15 = 3.3 ug.g-1 and the 100 g of ingested material would dose the individual with $3.3 \text{ ug.g-1} \times 100 \text{ g} \times 10^{-3} \text{ mg./ug} = 0.3 \text{ mg}$ free HCN, well below the average lethal dose of about 50 mg.

Similar calculations for Ammo technical, which has a larger value of K, would give still lower results in the above calculations.

Summary of Airborne Measurements and Their Meaning in Estimating Hazard Risks

Testing was conducted during the period of April 30-July 18 to evaluate the potential for hydrogen cyanide liberated from Ammo® insecticide to produce toxic concentration levels in work areas where the technical material is formulated, and also, in confined spaces where Ammo® insecticide products are handled and stored during transport and use.

HCN concentration measurements were made previously with directreading, short-term (1-minute) hydrogen cyanide detector tubes using
either Gastec or MSA. Continuous monitoring of HCN concentrations
made during detector tube sample taking, and also during Ammo® 2.5
EC product formulation (transfer of technical, rinsing of technical,
drums, product mixing and packing) and during warm room storage was
accomplished using a direct-reading MDA Compur 4100 Monitox HCN
Detector with a minimum detection level of 1 ppm HCN, and an audible
alarm sounding at HCN levels of 10 ppm and above.

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Test measurements were conducted in the head spaces of 55-gallon drums of Ammo® technical in actual formulation conditions (warehouse storage and heating to lower viscosity prior to formulating).

- o Readings at the manufacturing plant showed HCN concentrations ranging from 6 to 15 ppm in drums warehoused at 80°F, using MSA detector tubes.
- o Readings at the formulations plant showed HCN concentrations ranging from 40 to above 120 ppm in drums warmed to temperatures ranging from 41°C to 44°C, using Gastec detector tubes. As predicted by equilibrium studies, headspace concentrations of HCN increase with increased temperatures.

Test measurements were conducted in the head spaces of full containers and also in emptied containers of the formulated Ammo® 2.5 EC product to evaluate recommended disposal procedures.

- o HCN concentrations ranging from 40 ppm to 200 ppm in full containers using Gastec detector tubes.
- o Emptied, unrinsed and re-sealed 1-gallon containers develop HCN concentrations in the empty containers to approximately the same levels measured initially in full containers.
- o Rinsing empty Ammo® 2.5 EC containers with water greatly reduces the amount of HCN measurable in re-sealed containers.
- o Ventilating both rinsed and unrinsed empty Ammo® 2.5 EC containers by puncturing them and not replacing the caps as per label directions greatly reduces HCN concentrations.

HCN exposure of workers and work areas in the formulations plant was monitored during the normal formulation process.

- o Whenever full containers of Ammo® Technical, heated to 44°C, were opened to conduct HCN measurements in the head space, measurable HCN levels outside a 3-inch perimeter of the small bung opening could not be detected using the direct-reading MDA portable HCN detector. Values within the 3-inch perimeter ranged from 1 to 2 ppm.
- were opened to conduct HCN measurements in the head space, measurable HCN levels in the vicinity of the bung opening and in the breathing zones of the persons conducting the sampling could not be detected using the direct-reading MDA portable. HCN detector. Considering that the head space volumes of l-gallon containers are less than l-liter, and less than 8-liters in 55-gallon drums, the amount of HCN contained within would become rapidly diluted as it is emitted into the expansive open-air volume surrounding the drums, and as such is not considered to pose an occupational exposure hazard to workers during container emptying and rinsing operations where these products are formulated or mixed/loaded/applied.

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B

Non-detectable HCN concentrations were measured on workers who wore the direct-reading MDA portable HCN detectors during undrumming of 45 drums of Ammo® Technical and empty drum rinsing with solvent during the production of a batch of Ammo® 2.5 EC. Drum head space HCN levels ranged from 44 ppm to greater than 120 ppm. Gastec HCN detector tube measurements taken in the work area during both mixing and packing of the product in 1-gallon containers also yielded non-detectable results.

Simulations of spills of 55-gallon (Ammo® Technical) and 30-gallon (Ammo® 2.5 EC) quantities into poorly ventilated confined spaces of defined volume were conducted by proportionally weighing and introducing samples of these products into clean, dry, empty 55-gallon drums having an interior volume of 7.3 ft³. The defined volumes chosen for simulated tests were:

(a) A small storage room -1000 ft^3 .

(b) A 40-ft. commercial trailer van - 2560 ft³.

(c) A large storage room - 14,400 ft³.

Measurements made in the vapor spaces of these drums representing simulated liquid spill scenarios, at intervals from 16 to 180 hours, yielded HCN concentrations substantially lower than those found initially in the head spaces of containers from which they were drawn. The HCN levels in these simulations stabilized and did not increase substantially with time. The results obtained are tabulated below:

	SimulatedVolume	Simulated Material Spilled	Initial Head Space Concentration in Original Container ppm-HCN	Test Result from Simulation ppm-HCN
(a)	1,000 ft ³	30-Gal. Ammo® 2.5 EC	92	22-30
(b)	2,560 ft ³	30-Ga1. Ammo® 2.5 EC	92 29	8-15 Trace to 1.5
		55-Gal. Ammo® Technical	68	2-7
(c)	14,400 ft ³	30-Gal. Ammo® 2.5 EC	92	Less than 1
		55-Gal. Ammo® Technical	68	Less than []

It is likely that a vapor-liquid phase HCN equilibrium occurs since test drum samples in which the internal air volume was purged of KCN, for 10-minutes periods with air were found with time to slowly return to near previously measured HCN levels.

[2] (B) This testing demonstrated that in the unlikely event of a spill in a confined space, HCN concentrations immediately dangerous to life and health do not form. Therefore, worker entry into such spaces after a spill had occurred would not present a life or health threatening exposure.

Effects of Hydrogen Cyanide Overexposure

The joint federal OSHA/NIOSH Occupational Health Guidelines for Hydrogen Cyanide, issued September, 1978, states that the current OSHA standard for hydrogen cyanide is 10 parts of HCN per million parts of air (ppm) averaged over an eight-hour work shift. This is the OSHA regulated Permissible Exposure Limit, or PEL.

This Guideline, under "Summary of Toxicology," states:

A few inhalations of high concentrations of HCN may be followed by almost instantaneous collapse and cessation of respiration

- o 270 ppm HCN is immediately fatal to humans
- o 181 ppm is fatal after 10 minutes
- o 135 ppm is fatal after 30 minutes
- o 110 ppm may be fatal in 1 hour

At lower levels of exposure to HCN, the earliest symptoms of intoxication may include weakness, headache, confusion, and occasionally nausea and vomiting; respiratory rate and depth usually increase initially and at later stages become slow and gasping.

o Humans tolerate 45 to 54 ppm for 1/2 to 1 hour without immediate or delayed effects, while 18 to 36 ppm may result in some symptoms after an exposure of several hours.

Conclusion

Based on the results of this testing and monitoring of HCN levels, it can be determined that higher concentrations exist only within the small head space volume of product containers of Ammo® Technical and Ammo® 2.5 EC, and that evidence supporting a human health hazard risk presented by inhalation of hydrogen cyanide evolved from these products is negligible.

The information presented here confirms the Agency's (and FMC's) opinion as expressed in your letter of June 10, 1986 that the levels of HCN measured in Ammo products do not represent an undue hazard or changed product toxicity. FMC is proceeding to identify the likely sources of HCN in Ammo products and determine appropriate means to remove or stabilize them. Our plans are to attempt some of these potential solutions on a manufacturing scale and monitor the product. We will submit for EPA approval any changes in the manufacturing process, impurity profile or Confidential Statement of Formula as soon as we determine the utility of these methods.

If you have any questions about these findings or our plans, please do not hesitate to call me at 215-299-6662.

Respectfully,

Robert R. Stewart

Senior Registration Specialist

cc: Compliance Monitoring Division, EPA Washington